(12) EUROPEAN PATENT APPLICATION

(71) Applicant: **CHEVRON RESEARCH AND TECHNOLOGY COMPANY**
P.O. Box 7141, 525 Market Street
San Francisco, CA 94120-7141(US)

(72) Inventor: **Jossens, Lawrence W.**
914 Ventura
Albany, California 94707(US)
Inventor: **Santilli, Donald S.**
260 Piedmont Road
Larkspur, California 94939(US)
Inventor: **O'Rear, Dennis J.**
40 Upland Drive
Petaluma, California 94952(US)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte
Isartorplatz 6 Postfach 26 02 47
W-8000 München 2 (DE)

(54) Iso-olefin production and etherification process.

(57) A process for increasing iso-butylene and iso-pentene yield from a refinery naptha comprising contacting a olefinic naptha stream comprising C_5-C_9 olefins with a low acidic crystalline silicate catalyst at a pressure of less than 300 psig and a temperature of between about 500 to about 900 F to produce a product stream rich in iso-butylene and iso-pentene.

/02 → claims 27, 20

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BACKGROUND OF THE INVENTION

This invention relates to hydrocarbon conversion in a refinery. More specifically it relates to the production of iso-olefins from higher olefins contained in a refinery naptha.

In recent years, a major technical challenge presented to the petroleum refining industry has been the requirement to establish alternate processes for manufacturing high octane gasoline in view of the regulated requirement to eliminate lead additives as octane enhancers, reduce tailpipe and evaporative emissions, as well as the development of more efficient, higher compression ratio gasoline engines requiring higher octane fuel.

To meet these requirements the industry has developed non-lead octane boosters and has reformulated gasoline in response to the regulatory standards. While these and other approaches will fully meet the technical requirements of regulations requiring elimination of gasoline lead additives and allow the industry to meet the burgeoning market demand for high octane gasoline, the economic impact on the cost of gasoline is significant.

Accordingly, workers in the field have intensified their effort to discover new processes to manufacture the gasoline products required by the market place. One important focus of that research is a new process to produce high octane gasoline blended with lower aliphatic alkyl ethers as octane boosters and supplementary fuels. C_5-C_7 methyl alkyl ethers, especially methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) have been found particularly useful for enhancing gasoline octane. Therefore, improvements to the processes related to the production of these ethers are matters of high importance and substantial challenge to research workers in the petroleum refining arts.

Legislative mandates for a minimum oxygen content in motor fuels has led most refiners to consider adding MTBE, TAME and other high octane chemicals generally referred to as "oxygenates" to their gasoline production pool.

It is known that iso-butylene may be reacted with methanol over an acidic catalyst to provide methyl tertiary butyl ether (MTBE) and iso-amylenes may be reacted with methanol over an acidic catalyst to produce tertiary-amyl methyl ether (TAME).

However, iso-olefins often do not exist in refinery streams in the quantities required for desired MTBE and TAME production levels.

Further, at some locations in the U.S., olefin content of motor gasoline is limited using an analytical indicator such as Bromine Number. Due to the relatively high olefin content of some refinery streams, such as FCC gasoline, their use as blending stock for motor gasoline is constrained. FCC octane improvement often is achieved or accompanied by increased production of olefins, particularly olefins in the C_5 - C_9 range. The refiner is therefore limited in FCC performance by the mandated olefin limitation.

It is known that advanced octane oriented FCC catalysts or addition of octane additives to the FCC catalyst inventory can increase the production of iso-butylene. However, enhanced isobutylene production through the use of better octane catalysts is accomplished with increases in the olefinic content of the FCC gasoline along with parallel increases in other C_3 and C_4 gases; while the use of ZSM-5 based octane additives to enhance isobutylene yields does not reduce the olefinic concentration of the c_5 plug gasoline.

However, as described above, a large source of higher olefins of five carbons or more are typically found in gasoline from an FCC. Most commercial FCC gasolines contain olefins in the C_5 and higher range. These olefins are high octane components for gasoline and have often been produced themselves in synthesis reactions from lighter olefins.

In U.S. Patent No. 4,746,762 issued March 24, 1988 to Avidan, et al., light olefins are oligomerized to an olefinic gasoline.

U.S. Patent No. 5,004,852, issued April 2, 1991 to Harandi, describes a catalytic technique for upgrading olefin streams to gasoline streams rich in aromatics. In particular, it provides a continuous process for oligomerizing and aromatizing a feedstock containing light C4-olefins to produce C5 + hydrocarbons rich in C6-C10 aromatics, such as benzene, toluene, xylenes, tri-methylbenzenes and tetramethylbenzenes together with hydrogen and fuel gas.

U.S. Patent No. 4,282,085 to O'Rear et al., teaches the upgrading of a paraffinic distillate to C_4-C_5 olefins over a ZSM-5 type crystalline aluminosilicate catalyst.

U.S. Patent No. 5,026,936 issued June 25, 1991 to Leyshon, et al., teaches fluidized bed cracking and metathesis of butenes or higher olefins and/or paraffins for the production of ethylene and propylene with acidic ZSM-5 at: high space rate, between 5 to 2000, moderate pressures, -5 to 30 psig, and temperatures between 750 to 1472°F.

However, the production of iso-olefins from a refinery naptha, which naptha comprises olefins in the range of C_5-C_9, for feed to a MTBE or TAME unit has not been adequately addressed.

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An improved process for production of iso-butylene from a refinery stream is much desired.

SUMMARY OF THE INVENTION

5   We have discovered a process for producing iso-butylene and increasing the iso-pentene to total pentene ratio from an olefinic naptha comprising contacting an olefinic naptha stream comprising C_5-C_9 olefins with a low acidic crystalline silicate catalyst at a pressure of less than 300 psig and a temperature of between about 600°F to about 900°F to produce a stream comprising an increased amount of iso-butylene and an enhanced iso-pentene to total pentene ratio relative to the iso-butylene and iso-pentene/total

10   pentenes in the naptha. The practice of the present invention results in a reduction in olefinic content of the remaining olefinic naptha, relative to the olefinic content in the feed.

Among other factors, we have found that post-cracking an olefinic naptha with crystalline silicate under the above conditions, versus adding crystalline silicate to the FCC catalyst inventory results in higher overall iso-butylene production and higher iso-pentene to total pentene ratio due to reduced hydrogen transfer

15   associated with crystalline silicate relative to that of crystalline silicate mixed with FCC catalyst. Additional factors include extended residence time of the post cracking process and relatively low cracking temperature.

The practice of our discovery results in an increased overall yield of higher octane gasoline due to increased iso-olefins in the gasoline or available for etherification along with increased propylene available

20   for alkylation.

Surprisingly, we also found the C_5-C_9 olefins in olefinic FCC light gasoline to be preferentially converted by the process of the present invention to iso-butylene without the associated increases in C_5-plus olefin content; increase in n-butylene yield or propylene yield observed to result when the FCC catalyst inventory is switched to a better octane catalyst for the purpose of enhancing isobutylene yields. Further to our

25   surprise, we discovered that iso-butylene and iso-pentene selectivity and catalyst activity do not significantly diminish when the process of our present invention is carried out at pressures above atmospheric pressure.

Also, the production of iso-butylene by the iso-olefin production process described in this invention is accomplished with just trace, if any, production of butadiene along with the transformation of pentadienes

30   such that the cracked olefinic gasoline contains substantially less pentadienes and little if any butadienes, relative to the olefinic feed naptha. The production of essentially butadiene-free iso-butylene and essentially pentadiene-free iso-pentenes obviate the need for diolefin clean-up steps normally required before either MTBE and/or TAME production units.

35   ## DETAILED DESCRIPTION OF THE INVENTION

PROCESS

The present invention is a process which combines the use of a particular feedstream, in a reaction in

40   the presence of a particular catalyst, to yield the advantageous result of increasing the production of particular components in a product stream. The product stream, then having more desirable levels of particular components, may then be further processed.

In one embodiment, the olefinic feed to our process is FCC gasoline from an FCC unit. A range of such FCC gasolines, comprising olefins in the range of C_5 to C_9, are effectively processed by the present

45   process, but our best iso-butene and iso-pentene production results were accomplished when the FCC gasoline had a boiling range of between about 65°F to about 340°F. Other olefinic naphthas like pyrolysis naphthas, naphthas from the production of ethylene and propylene, coker naphthas or naphthas from propylene oligomerization can be used.

In another embodiment, following separation of a butylene rich stream resulting from the highly

50   selective reaction, the stream comprising normal and iso-butylenes are fed to a MTBE unit. In another embodiment, following separation of a pentene-rich stream, the stream comprising iso-pentenes are feed to a TAME unit.

We have further found the crystalline silicate used in the conversion of naptha olefins to be highly effective in the conversion of propylene and n-butylenes to iso-butylene. We have seen particularly good

55   results in iso-butylene production when the ratio of recycled n-butylene to total feed stream is between about 2% to about 20%.

Accordingly, in still another embodiment of our invention, propylene from the reaction of the naptha olefins, or alternatively propylene from any source, is recycled back to be blended with incoming olefinic

naptha feed to the crystalline silicate-containing reactor. Propylene recycle ratios relative to total feed to the crystalline silicate-containing reactor in the range of about 2% to about 20% are preferred.

In yet another embodiment, unreacted butenes comprised chiefly of n-butylene, from the MTBE unit are returned to the crystalline silicate-containing reactor where at least a portion of the n-butylene is converted
5 to iso-butylene.

In addition to the enhanced iso-butylene production achieved from the post-cracking of an olefinic naptha, it was found that the ratio of iso to normal pentenes increased, and that cracking an olefinic naptha stream did not result in a decrease of iso-pentenes, which are required in the production of TAME. Therefore, in another embodiment of this invention, normal pentenes from TAME production or from
10 oligomerization are fed along with the olefinic gasoline to the silicalite-containing reactor unit resulting in enhanced iso-pentene yields over that achieved by processing the olefinic naptha stream without such a recycle.

In yet another embodiment, fractionating a C_5 to C_7 cut from the iso olefin enriched product stream exiting the crystalline silicate-containing reactor yields an iso-olefin rich stream which can be dispropor-
15 tionated with ethylene and/or propylene, which may be from any source including FCC produced ethylene and/or propylene, to yield additional iso-butylene and iso-pentene. In turn, the resulting normal butylene from the disproportionation unit can be either recycled or alkylated while iso-butylene can be used for MTBE production and iso-pentene for TAME. In accordance with our invention, a process is carried out for increasing iso-butylene and enhanced iso-pentene to total pentene ratio from a refinery naphtha. The
20 process comprises the steps of contacting a olefinic naptha stream comprising C_5-C_9 olefins with a crystalline silicate catalyst at a temperature of between about 500°F to about 900°F to produce an iso-butylene and iso-pentene rich product stream comprising iso-butylene and iso-pentene, saturated butanes and propylene. By "iso-butylene rich and iso-pentene rich" we mean the total amount of iso-butylene in the product stream relative to the total amount of iso-butylene in the naphtha and iso-pentene/total pentene ratio
25 in the product stream relative to iso-pentene/total pentene ratio in the naptha is increased.

While not wishing to be bound to any particular theory of operation, we believe that post-cracking an olefinic naptha with crystalline silicate under the above conditions, versus adding crystalline silicate to the FCC catalyst inventory results in higher overall iso-butylene production due to reduced hydrogen transfer associated with crystalline silicate relative to that of crystalline silicate mixed with FCC catalyst. This is most
30 likely because if intermediate hydrogen deficient products are formed in the FCC, the faujasite type FCC catalyst will promote hydride transfer to form hydrogen saturated compounds.

Further to our surprise, we discovered that iso-butylene selectivity and catalyst activity do not significantly diminish when the process of our present invention is carried out at pressures above atmospheric pressure. While not wishing to limit our invention in any way depending on any theory, we
35 believe disproportionation, iso/normal equilibration of butylene and pentene along with oligomerization reactions occurring in the contacting of a olefinic naptha with a crystalline silicate at the reaction conditions as claimed in our invention combine to enhance the production of iso-butylene and iso-pentenes.

While it is recognized that disproportionation can switch the carbon groups next to the double bond to, for example, produce butene, we have found the reaction conditions under which our invention operates
40 over crystalline silicate actually enhances the needed branching required to produce iso-butylene and iso-pentene.

CATALYST

45 The reactor utilized in the practice of the present invention may be a moving bed or fluidized bed and is preferably a fixed-bed reactor. The catalyst used in the reactor is a crystalline silicate. The crystalline silicate component of the catalyst of the present invention is generally referred to herein as silicate or crystalline silicate, but also is commonly referred to as a zeolite.

The silicate of the catalyst of the present invention preferably is low in acidity. The low acidity may be
50 achieved by a combination of low aluminum content in the silicate and the use of low amounts of alkali and/or the use of alkaline earth metals. The silicate component of the catalyst preferably is included in a matrix or binder to form the finished catalyst, as described hereinbelow. Preferably, the finished catalyst is of low acidity.

The present invention uses an intermediate pore size crystalline silicate material having a high silica to
55 alumina ratio. One preferred material is "silicalite" or high ratio silica to alumina form of ZSM-5.

Table 1 below reports the X-ray diffraction pattern for ZSM-5 as given in the Argauer patent (USP 3,702,886).

TABLE 1

Interplanar Spacing d(A)	Relative Intensity
11.1±0.2	s.
10.0±0.2	s.
7.4±0.15	w.
7.1±0.15	w.
6.3±0.1	w.
6.04 ±0.1	w.
5.97	w.
5.56±0.1	w.
5.01±0.1	w.
4.60±0.08	w.
4.25±0.08	w.
3.85±0.07	v.s.
3.71±0.05	s.
3.04±0.03	w.
2.99±0.02	w.
2.94±0.02	w.

Also as reported in the Argauer '886 patent, the values in Table 1 were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a scintillation counter spectrometer with a strip chart pen recorder was used. The peak heights, I, and the positions as a function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these, the relative intensities, $100 \, I/I_o$, where I_o is the intensity of the strongest line or peak, and d (obs.), the interplanar spacing in A, corresponding to the recorded lines, were calculated. In Table 1, the relative intensities are given in terms of the symbols s. = strong, m. = medium, m.s. = medium strong, m.w. = medium weak and v.s. = very strong. It should be understood that this X-ray diffraction pattern is characteristic of all the species of ZSM-5 compositions. Ion exchange of the sodium ion with cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the silicon to aluminum ratio of the particular sample, as well as if it had been subjected to thermal treatment.

ZSM-5 is regarded by many to embrace "silicalite" as disclosed in U.S. Patent No. 4,061,724 to Grose et al. For ease of reference herein, silicalite is referred to as a ZSM-5-type material with a high silica to alumina ratio and is regarded as embraced within the ZSM-5 X-ray diffraction pattern. The silica to alumina ratio is on a molar basis of silica (SiO_2) to alumina (Al_2O_3).

Various references disclosing silicalite and ZSM-5 are provided in U.S. Patent No. 4,401,555 to Miller. These references include the aforesaid U.S. Patent No. 4,061,724 to Grose et al.; U.S. Patent Reissue No. 29,948 to Dwyer et al.; Flanigan et al., Nature, 271, 512-516 (February 9, 1978) which discusses the physical and adsorption characteristics of silicalite; and Anderson et al., J. Catalysis 58, 114-130 (1979) which discloses catalytic reactions and sorption measurements carried out on ZSM-5 and silicalite. The disclosures of these references and U.S. Patent No. 4,401,555 are incorporated herein by reference, particularly including their disclosures on methods of making high silica to alumina crystalline silicates having an X-ray diffraction pattern in substantial accord with Table 1.

Other crystalline silicates which can be used in the process of the present invention include those as listed in U.S. Patent No. 4,835,336; namely: ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, and other similar materials.

ZSM-5 is more particularly described in U.S. Patent No. 3,702,886 and U.S. Patent Reissue No. 29,948, the entire contents of which are incorporated herein by reference.

ZSM-11 is more particularly described in U.S. Patent No. 3,709,979 the entire contents of which are incorporated herein by reference. Bibby et al., Nature, 280, 664-665 (August 23, 1979) reports the preparation of a crystalline silicate called "silicalite-2".

ZSM-12 is more particularly described in U.S. Patent No. 3,832,449, the entire contents of which are incorporated herein by reference.

ZSM-22 is more particularly described in U.S. Patent Nos. 4,481,177, 4,556,477 and European Patent No. 102,716, the entire contents of each being expressly incorporated herein by reference.

ZSM-23 is more particularly described in U.S. Patent No. 4,076,842, the entire contents of which are incorporated herein by reference.

ZSM-35 is more particularly described in U.S. Patent No. 4,016,245, the entire contents of which are incorporated herein by reference.

ZSM-38 is more particularly described in U.S. Patent No. 4,046,859, the entire contents of which are incorporated herein by reference.

ZSM-48 is more particularly described in U.S. Patent No. 4,397,827 the entire contents of which are incorporated herein by reference.

Of these, ZSM-5, ZSM-11, ZSM-22 and ZSM-23 are preferred. ZSM-5 is most preferred for use in the catalyst of the present invention.

Additionally, zeolites SSZ-20, SSZ-23 and SSZ-32 are preferred. SSZ-20 is disclosed in U.S. Patent No. 4,483,835, and SSZ-23 is disclosed in U.S. Patent No. 4,859,442, both of which are incorporated herein by reference.

The crystalline silicate may be in the form of a borosilicate, where boron replaces at least a portion of the aluminum of the more typical aluminosilicate form of the silicate. Borosilicates are described in U.S. Patent Nos. 4,268,420; 4,269,813; and 4,327,236 to Klotz, the disclosures of which patents are incorporated herein, particularly that disclosure related to borosilicate preparation.

In a borosilicate catalyst used in the process of the present invention, the preferred crystalline structure is that of ZSM-5, in terms of X-ray diffraction pattern. Boron in the ZSM-5 type borosilicates takes the place of aluminum that is present in the more typical ZSM-5 crystalline aluminosilicate structures. Borosilicates contain boron in place of aluminum, but generally there is some trace amounts of aluminum present in crystalline borosilicates.

Still further crystalline silicates which can be used in the present invention are ferrosilicates, as disclosed for example in U.S. Patent No. 4,238,318, gallosilicates, as disclosed for example in U.S. Patent No. 4,636,483, and chromosilicates, as disclosed for example in U.S. Patent No. 4,299,808.

Thus various high silica content silicates (silicates having a high ratio of silica to other constituents) can be used as the crystalline silicate component of the catalyst of the present invention.

Borosilicates and aluminosilicates are preferred silicates for use in the present invention. Aluminosilicates are the most preferred. Silicalite is a particularly preferred aluminosilicate for use in the catalyst of the present invention.

As synthesized, silicalite (according to U.S. Patent No. 4,061,724) has a specific gravity at 77°F of 1.99 ± 0.05 g/cc as measured by water displacement. In the calcined form (1112°F in air for one hour), silicalite has a specific gravity of 1.70 ± 0.05 g/cc. With respect to the mean refractive index of silicalite crystals, values obtained by measurement of the as synthesized form and the calcined form (1112°F in air for one hour) are 1.48 ± 0.01 and 1.39 ± 0.01, respectively. The X-ray powder diffraction pattern of silicalite (1112°F calcination in air for one hour) has six relatively strong lines (i.e., interplanar spacings). They are set forth in Table 2 ("S"-strong, and "VS"-very strong):

TABLE 2

d-A	Relative Intensity
11.1 ±	0.2VS
10.0 ±	0.2VS
3.85 ±	0.07VS
3.82 ±	0.07S
3.76	0.05S
3.72 ±	0.05S

Table 3 shows the X-ray powder diffraction pattern of a typical silicalite composition containing 51.9 mols of SiO_2 per mol of tetrapropyl ammonium oxide [$(TPA)_2O$], prepared according to the method of U.S. Patent No. 4,061,724, and calcined in air at 1112°F for one hour.

TABLE 3

d a	Relative Intensity	d-A	Relative Intensity
11.1	100	4.35	5
10.02	64	4.25	7
9.73	16	4.08	3
8.99	1	4.00	3
8.04	0.5	3.85	59
7.42	1	3.82	32
7.06	0.5	3.74	24
6.68	5	3.71	27
6.35	9	3.64	12
5.98	14	3.59	0.5
5.70	7	3.48	3
5.57	8	3.44	5
5.36	2	3.34	11
5.11	2	3.30	7
5.01	4	3.25	3
4.98	5	3.17	0.5
4.86	0.5	3.13	0.5
4.60	3	3.05	5
4.44	0.5	2.98	10

Silicalite crystals in both the "as synthesized" and calcined forms are generally orthorhombic and have the following unit cell parameters: a = 20.05Å, b = 19.86Å, c = 13.36Å (all values ±0.1A).

The pore diameter of silicalite is about 6Å and its pore volume is 0.18 cc/gram as determined by adsorption. Silicalite adsorbs neopentane (6.2Å kinetic diameter) slowly at ambient room temperature. The uniform pore structure imparts size-selective molecular sieve properties to the composition, and the pore size permits separation of p-xylene from o-xylene, m-xylene and ethyl-benzene as well as separations of compounds having quaternary carbon atoms from those having carbon-to-carbon linkages of lower value (e.g., normal and slightly branched paraffins).

The crystalline silicates of U.S. Patent Reissue No. 29,948 (Reissue of USP 3,702,886 to Argauer) are disclosed as having a composition, in the anhydrous state, as follows:

$$0.9 \pm 0.2 \, [xR_2O + (1 - x)M_{2/n}O]: < .005$$
$$Al_2O_3 :> 1 \, SiO_2$$
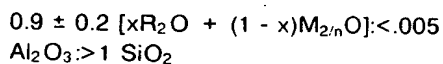
where M is a metal, other than a metal of Group IIIA, n is the valence of said metal, R is an alkyl ammonium radical, and x is a number greater than 0 but not exceeding 1. The crystalline silicate is characterized by the X-ray diffraction pattern of Table 1, above.

The crystalline silicate polymorph of U.S. Patent No. 4,073,865 to Flanigen et al. is related to silicalite and, for purposes of the present invention, is regarded as being in the ZSM-5 class. The crystalline silicate exhibits the X-ray diffraction pattern of Table 4.

TABLE 4

d(A)	Intensity
11.14	91
10.01	100
9.75	17
8.99	1
8.01	0.5
7.44	0.5
7.08	0.2
6.69	4
6.36	6
5.99	10
5.71	5
5.57	5
5.37	1
5.33	1
5.21	0.3
5.12	1.5
5.02	3
4.97	6
4.92	0.6
4.72	0.5
4.62	2
4.47	0.6
4.36	3
4.25	4
4.13	0.5
4.08	1.5
4.00	3
3.85	44
3.82	25
3.71	21
3.65	5
3.62	5
3.59	1
3.48	1.5
3.45	3
3.44	3
3.35	3
3.31	5
3.25	1.5
3.23	0.8
3.22	0.5

According to the August 1979 Nature reference cited above, a silicalite-2 precursor can be prepared using tetra-n-butylammonium hydroxide only, although adding ammonium hydroxide or hydrazine hydrate as a source of extra hydroxyl ions increases the reaction rate considerably. It is stable at extended reaction times in a hydrothermal system. In an example preparation, 8.5 mol SiO_2 as silicic acid (74% SiO_2) is mixed with 1.0 mol tetra-n-butylammonium hydroxide, 3.0 mol NH_4OH and 100 mol water in a steel bomb and heated at 338°F for three days. The precursor crystals formed are ovate in shape, approximately 2-3 microns long and 1-1.5 microns in diameter. It is reported that the silicalite-2 precursor will not form if Li, Na, K, Rb or Cs ions are present, in which case the precursor of the U.S. Patent No. 4,061,724 silicalite is formed. It is also reported that the size of the tetraalkylammonium ion is critical because replacement of the tetra-n-butylammonium hydroxide by other quaternary ammonium hydroxides (such as tetraethyl, tetrapropyl, triethylpropyl, and triethylbutyl hydroxides) results in amorphous products. The amount of Al present in silicalite-2 depends on the purity of the starting materials and is reported as being less than 5

ppm. The precursor contains occluded tetraalkylammonium salts which, because of their size, are removed only by thermal decomposition. Thermal analysis and mass spectrometry show that the tetraalkylammonium ion decomposes at approximately 572°F and is lost as the tertiary amine, alkene and water. This is in contrast to the normal thermal decomposition at 392°F of the same tetraalkylammonium salt in air.

The Nature article further reports that the major differences between the patterns of silicalite and silicalite-2 are that peaks at 9.06, 13.9, 15.5, 16.5, 20.8, 21.7, 22.1, 24.4, 26.6 and 27.0° 2θ (CuK alpha radiation) in the silicalite X-ray diffraction pattern are absent from the silicalite-2 pattern. Also, peaks at 8.8, 14.8, 17.6, 23.1, 23.9 and 29.9 degrees are singlets in the silicalite-2 pattern rather than doublets as in the silicalite pattern. These differences are reported as being the same as those found between the aluminosilicate diffraction patterns of orthorhombic ZSM-5 and tetragonal ZSM-11. Unit cell dimensions reported as calculated on the assumption of tetragonal symmetry for silicalite-2 are a = 20.04Å; b = 20.04Å; c = 13.38Å. The measured densities and refractive indices of silicalite-2 and its precursor are reported as 1.82 and 1.98 g/cc and 1.41 and 1.48 respectively.

For purposes of the present invention, silicalite is regarded as being in the ZSM-5 class, alternatively put, as being a form of ZSM-5 having a high silica to alumina ratio; silicalite-2 is regarded as being in the ZSM-11 class.

The preparation of crystalline silicates of the present invention generally involves the hydrothermal crystallization of a reaction mixture comprising water, a source of silica, and an organic templating compound at a pH of 10 to 14. Representative templating moieties include quaternary cations such as XR_4 where X is phosphorous or nitrogen and R is an alkyl radical containing from 2 to 6 carbon atoms, e.g., tetrapropylammonium hydroxide (TPA-OH) or halide, as well as alkyl hydroxyalkyl compounds, organic amines and diamines, and heterocycles such as pyrrolidine.

When the organic templating compound (i.e., TPA-OH) is provided to the system in the hydroxide form in sufficient quantity to establish a basicity equivalent to the pH of 10 to 14, the reaction mixture may contain only water and a reactive form of silica as additional ingredients. In those cases in which the pH must be increased to above 10, ammonium hydroxide or alkali metal hydroxides can be suitably employed for that purpose, particularly the hydroxides of lithium, sodium and potassium. The ratio: R^+ to the quantity R^+ plus M^+, where R^+ is the concentration of organic templating cation and M^+ is the concentration of alkali metal cation, is preferably between 0.7 and 0.98, more preferably between 0.8 and 0.98, most preferably between 0.85 and 0.98.

The source of silica in the reaction mixture can be wholly, or in part, alkali metal silicate. Other silica sources include solid reactive amorphous silica, e.g., fumed silica, silica sols, silica gel, and organic orthosilicates. One commercial silica source is Ludox AS-30, available from DuPont.

Aluminum, usually in the form of alumina, is easily incorporated as an impurity into the crystalline silicate. Aluminum in the crystalline silicate contributes acidity to the catalyst, which is undesirable. To minimize the amount of aluminum, care should be exercised in selecting a silica source with a minimum aluminum content. Commercially available silica sols can typically contain between 500 and 700 ppm alumina, whereas fumed silicas can contain between 80 and 2000 ppm of alumina impurity. As explained above, the silica to alumina molar ratio in the crystalline silicate of the catalyst used in the present invention is preferably greater than 200:1.

The quantity of silica in the reaction system is preferably between about 1 and 10 mols SiO_2 per mol-ion of the organic templating compound. Water should be generally present in an amount between 20 and 700 mol per mol-ion of the quaternary cation. The reaction preferably occurs in an aluminum-free reaction vessel which is resistant to alkali or base attack, e.g., Teflon.

In forming the final catalyst used in the present invention, the crystalline silicate is preferably bound with a matrix. The term "matrix" includes inorganic compositions with which the silicate can be combined, dispersed, or otherwise intimately admixed. Preferably, the matrix is not catalytically active in a hydrocarbon cracking sense, i.e., contains substantially no acid sites. Satisfactory matrices include inorganic oxides. Preferred inorganic oxides include alumina, silica, alumina-alumina-phosphates, naturally occurring and conventionally processed clays, for example bentonite, kaolin, sepiolite, attapulgite and halloysite. Preferred matrices are substantially non-acidic and have little or no cracking activity. Silica matrices and also alumina matrices are especially preferred. We have found that the use of a low acidity matrix, more preferably a substantially non-acidic matrix, is advantageous in the catalyst of the present invention.

Compositing the crystalline silicate with an inorganic oxide matrix can be achieved by any suitable method wherein the silicate is intimately admixed with the oxide while the latter is in a hydrous state (for example, as a hydrous salt, hydrogel, wet gelatinous precipitate, or in a dried state, or combinations thereof). A convenient method is to prepare a hydrous mono or plural oxide gel or cogel using an aqueous solution of a salt or mixture of salts (for example, aluminum sulfate and sodium silicate). Ammonium

hydroxide carbonate (or a similar base) is added to the solution in an amount sufficient to precipitate the oxides in hydrous form. Then, the precipitate is washed to remove most of any water soluble salts and it is thoroughly admixed with the silicate which is in a finely divided state. Water or a lubricating agent can be added in an amount sufficient to facilitate shaping of the mix (as by extrusion).

5   A preferred crystalline silicate for use in the catalyst of the present invention is ZSM-5 having a high silica to alumina ratio, which, for convenience, is frequently referred to herein as "silicalite". Assuming that the only crystalline phase in the silicalite prep is silicalite, the silicalite preferably has a percent crystallinity of at least 80%, more preferably at least 90%, most preferably at least 95%. To determine percent crystallinity, an X-ray diffraction (XRD) pattern of the silicalite is made and the area under the eight major
10 peaks is measured in the angle interval between 20.5 and 25.0 degrees. Once the area under the curve is calculated, it is compared with the area under the curve for a 100% crystalline standard for silicalite.

The preferred crystallite size of the crystalline silicate is less than 10 microns, more preferably less than 5 microns, still more preferably less than 2 microns, and most preferably less than 1 micron. When a crystallite size is specified, preferably at least 70 wt. % of the crystallites are that size, more preferably at
15 least 80 wt. %, most preferably 90 wt. %. Crystallite size can be controlled by adjusting synthesis conditions, as known to the art. These conditions include temperature, pH, and the mole ratios H_2O/SiO_2, R^+/SiO_2, and M^+/SiO_2, where R^+ is the organic templating cation and M^+ an alkali metal cation. For small crystallite size, i.e., less than 10 microns, typical synthesis conditions are listed below:

20

	Preferred	More Preferred	Most Preferred
Temperature, °F	176-392	144-356	212-302
pH	12-14	12.5-14	13-13.5
$H_2O/SiO2$	5-100	10-50	10-40
R^+/SiO_2	0.1-1.0	0.1-0.5	0.2-0.5
M^+/SiO_2	0.01-0.3	0.01-0.15	0.01-0.08

25

30 Other techniques known to the art, such as seeding with silicate crystals, can be used to reduce crystallite size.

The crystalline silicate component of the catalyst of the present invention has an intermediate pore size. By "intermediate pore size" as used herein is meant an effective pore aperture in the range of about 5 to 6.5Å when the silicate is in the H-form. Crystalline silicates having pore apertures in this range tend to have unique molecular sieving characteristics. Unlike small pore crystalline silicates or zeolites such as erionite,
35 they will allow hydrocarbons having some branching into the zeolitic void spaces. Unlike large pore zeolites such as the faujasites, they can differentiate between n-alkanes and slightly branched alkanes on the one hand and larger branched alkanes having, for example, quarternary carbon atoms.

The effective pore size of the crystalline silicates or zeolites can be measured using standard adsorption techniques and hydrocarbonaceous compounds of known minimum kinetic diameters. See
40 Breck, Zeolite Molecular Sieves, 1974 (especially Chapter 8) and Anderson et al., J.Catalysis 58, 114 (1979), both of which are incorporated by reference.

Intermediate pore size crystalline silicates or zeolites in the H-form will typically admit molecules having kinetic diameters of 5 to 6Å with little hindrance. Examples of such compounds (and their kinetic diameters in Angstroms) are: n-hexane (4.3), 3-methylpentane (5.5), benzene (5.85), and toluene (5.8). Compounds
45 having kinetic diameters of about 6 to 6.5Å can be admitted into the pores, depending on the particular zeolite, but do not penetrate as quickly and in some cases, are effectively excluded (for example, 2,2-dimethylbutane is excluded from H-ZSM-5). Compounds having kinetic diameters in the range of 6 to 6.5Å include: cyclohexane (6.0), m-xylene (6.1) and 1,2,3,4-tetramethylbenzene (6.4). Generally, compounds having kinetic diameters of greater than about 6.5Å cannot penetrate the pore apertures and thus cannot be
50 adsorbed in the interior of the zeolite. Examples of such larger compounds include: o-xylene (6.8), hexamethylbenzene (7.1), 1,3,5-trimethylbenzene (7.5), and tributylamine (8.1).

The preferred effective pore size range is from about 5.3 to about 6.2Å. ZSM-5, ZSM-11 and silicalite, for example, fall within this range.

In performing adsorption measurements to determine pore size, standard techniques are used. It is
55 convenient to consider a particular molecule as excluded if it does not reach at least 95% of its equilibrium adsorption value on the zeolite in less than about 10 minutes (P/Po = 0.5 25°C).

Examples of intermediate pore size zeolites include silicalite and members of the ZSM series such as ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, SSZ-20, SSZ-23 and SSZ-32.

EXAMPLE I

An FCC light gasoline feed recovered from an operating refinery FCC unit, "FCC Unit A," and having the following properties was used to demonstrate the process of this invention:

Table I

Feed Composition, "FCC Unit A"

Composition, wt. %

Methane	0.0
Ethylene	0.0
Ethane	0.0
Propylene	0.0
Propane	0.0
i-Butane	0.61
n-Butane	0.53
1-Butene	0.34
i-Butylene	0.40
t-2-Butene	1.01
c-2-Butene	1.13
3M-1 Butene	0.28
1-Pentene	0.85
2M-1 Butene	1.93
t-2 Pentene	2.67
c-2 Pentene	1.33
2M-2 Butene	4.03

Simulated Distillation, wt. % (D2887)

wt. %	F
St	15
5%	19
30%	134
50%	194
95%	359
99%	428

Yield, wt. %

C5-180°F	42.16
180-250°F	24.92
250 F+	28.91
*C5+	95.99
Ratio	0.56

(iso-C_5 Olefins/total C_5 Olefins)

*C5+ Breakdown, wt. %

Paraffins	39.6
Olefins	29.3
Naphthanes	9.2
Aromatics	21.9

The feed having the properties shown in Table I was passed over a catalyst consisting of 100% Conteka silicalite with a 400 SiO_2/Al_2O_3 ratio at temperatures between 750 and 850°F and at total

pressures between 0 to 150 psig (14.7 to 164.7 psia).

The results listed in Table II show the increase in the isobutylene yield along with the enhancement of iso-C_5 olefins to total C_5 olefins during reaction over the silicalite catalyst.

Table II

Feed	Light Gasoline	Light Gasoline	Light Gasoline	Light Gasoline
Run-Hours	38-28	38-97	38-433	38-601
Temperature, °F	750.00	750.00	800.00	830.00
WSHV	2.93	3.47	3.44	3.44
Pressure, psig	20.00	20.00	20.00	20.00
Yields, wt. %				
Hydrogen	0.01	0.00	0.00	0.00
Methane	0.00	0.00	0.01	0.00
Ethylene	0.45	0.09	0.12	0.01
Ethane	0.00	0.00	0.12	0.12
Propylene	3.60	2.50	0.01	0.01
Propane	0.70	0.08	3.67	3.24
i-Butane	1.58	0.64	0.07	0.03
n-Butane	1.15	0.59	0.65	0.52
1-Butene	0.83	0.77	0.65	0.63
i-Butene	3.39	2.97	0.97	0.89
t-2-Butene	1.66	1.50	3.51	2.96
c-2-Butene	1.18	1.14	1.73	1.78
Butadiene	0.00	0.00	1.32	1.14
Yield, wt. %			0.00	0.00
C_5-180F	40.86	45.67	44.75	48.84
180-250F	8.26	19.01	19.16	17.47
250F+	26.32	25.01	23.37	22.37
C_5+	85.43	89.69	87.28	88.68
C_5 Plus Vol %				
Paraffins	46.6	43.6	42.8	42.8
Olefins	15.6	20.2	22.8	23.3
Naphthanes	10.	9.2	9.4	8.8
Aromatics	27.8	27.0	25.1	25.2
Ratio	0.71	0.70	0.69	0.68
(iso-C_5 Olefin/Total C_5 Olefin)				

EXAMPLE II

To demonstrate the utility of this invention in treating a feed stream containing recycle propylene and/or recycle n-butenes, an FCC light gasoline feed containing propylene and an FCC light gasoline feed containing n-butene were reacted over the silicalite catalyst. The results listed in Table III show the results with the normal olefins added to the feed stream.

Table III

Feed	Light Gasoline	Light Gasoline + 8% Propylene	Light Gasoline + 20% 2-Butene	Light Gasoline + 6% Propylene	Light Gasoline + 6.4% 2-Butene	Light Gasoline 2-Butene
Run-Hours	38-720	38-745	38-769	40-478	40-621	40-648
Temperature, °F	850.00	850.00	850.00	780.00	800.00	800.00
WHSV of light gasoline	3.32	3.34	3.32	2.10	2.20	2.17
Pressure, psig	0.00	0.00	0.00	68.00	66.00	61.00
Yields, wt. % of light gasoline						
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00
Methane	0.01	0.01	0.01	0.01	0.01	0.02
Ethylene	0.17	0.24	0.18	0.10	0.10	0.08
Ethane	0.01	0.01	0.01	0.01	0.01	0.01
Propylene	3.59	9.95	4.85	3.74	3.11	2.43
Propane	0.07	0.17	0.08	0.20	0.12	0.08
i-Butane	0.63	0.55	0.58	0.74	0.62	0.53
n-Butane	0.62	0.61	0.94	0.75	0.90	0.62
1-Butene	0.94	1.34	4.78	0.97	1.29	0.75
i-Butylene	2.73	4.10	4.62	3.25	3.21	2.53
t-2-Butene	1.72	2.24	9.00	1.98	2.54	1.55
c-2-Butene	1.45	1.65	5.51	1.50	1.72	1.05
Butadiene	0.00	0.00	0.00	0.00	0.00	0.00
C_5-180F	49.02	44.29	40.00	46.26	51.28	45.80
180-250F	17.47	18.30	21.40	19.93	18.70	19.20
250F+	21.58	24.54	28.05	26.49	22.79	25.30
C_5+	88.07	87.13	89.45	92.69	92.78	90.40
iso-C_5 Olefins / total C_5 Olefins	0.66	0.67	0.66	0.69	0.71	0.68

EXAMPLE III

To demonstrate the utility of this invention in treating a feed stream containing recycled normal pentenes for the production of additional iso-pentenes, an FCC light gasoline feed containing additional 1-pentene was reacted over the silicalite catalyst. The results listed in Table IV show the enhanced iso-pentene yield with 1-pentene added to the feed stream.

Table IV

EFFECT OF RECYCLED n-PENTENE

Feed	Light Gasoline	Light Gasoline + 13.4% 1-Pentene
Run-Hours	40-958	40-1150
Temperature, °F	850	850
WHSV of Light Gasoline	1.9	1.6
Pressure, psig	140	148

Yields, wt. % of Light Gasoline

H_2		
Methane	0.00	0.00
Ethylene	0.08	0.09
Ethane	0.16	0.12
Propylene	0.10	0.13
Propane	2.65	2.30
i-Butane	0.24	0.19
n-Butane	0.64	0.53
1-Butene	0.73	0.59
isobutylene	0.80	0.91
t-2 Butene	2.56	2.47
C-2 Butene	1.46	1.70
Butadiene	1.14	1.19
	0.00	0.00

Pentene Yields,
wt. % of Light Gasoline

3M-1 Butene	0.33	1.14
1-Pentene	0.49	1.27
2M-1 Butene	2.10	5.47
t2-Pentene	1.43	3.69
C2-Pentene	0.80	2.04
2M-2 Pentene	4.01	10.85

iso-C_5 Olefins/total C_5 Olefins	0.70	0.71

EXAMPLE IV

Selective partial hydrogenation of the pentene stream used in TAME production is usually required to remove pentadienes. The process stated in this invention has the added advantage of reducing pentadienes. Reduced pentadiene levels were demonstrated by processing an additional light gasoline derived from "FCC Unit B". Properties of "FCC Unit B" light gasoline are tabulated in Table V and the resulting product from passing the feed of Table V over silicalite with a 400 SiO_2/Al_2O_3 ratio are listed in Table VI. The gas chromatographic techniques used to identify and quantify gasoline components were modified so as to include pentadienes in this example. As shown in Table VI, the pentadiene levels have been greatly reduced.

Table V

FEED COMPOSITION, "FCC UNIT B"

Composition, wt. %

Methane	0.0
Ethylene	0.0
Ethane	0.0
Propylene	0.0
Propane	—
Iso Butane	0.13
n-Butane	0.41
1-Butene	0.27
Iso Butene	0.22
t2-Butene	1.23
C2-Butene	1.42
3M-1 Butene	0.35
1-Pentene	1.23
2M-1 Butene	2.44
Isoprene	0.06
T2-Pentene	3.62
C2-Pentene	2.05
2M-2 Butene	5.41
1t3 Pentadiene	0.04
1c3 Pentadiene	0.03
Cyclopentadiene	0.03
Iso Pentenes/Total Pentenes	0.54

Simulated Distillation, wt. % (D2887)

Wt. %	°F
ST	23
5	94
30	135
50	175
95	330
99	397

Table VI

Run-Hours	41-240
Temperature, °F	750
WHSV	2.9
Pressure psig	0.
Yields, wt. %	
Hydrogen	0.0
Methane	0.0
Ethylene	0.05
Ethane	0.0
Propylene	2.42
Propane	.02
Iso-Butane	0.17
n-Butane	0.46
1-Butene	0.92
Iso-Butene	3.05
t-2-Butene	1.70
c-2-Butene	1.25
Pentadienes wt. %	
Isoprene	<0.002
1-t-3-Pentadiene	<0.001
1-c-3-Pentadiene	<0.002
Cyclopentadiene	<0.001
Isopentenes/Total Pentenes	0.72

To demonstrate the effectiveness of a low acidic ZSM-5 material used in this process versus an acidic ZSM-5 material, a 46 silica to alumina molar ratio ZSM-5 material was used to process the light gasoline from "FCC Unit B". As demonstrated in Table VII, the acidic ZSM-5 is apparently not as active as the 400 silica to alumina ZSM-5 used to demonstrate this process. The acidic material required a higher temperature to come on stream, 800 versus 750° F, and fouled rapidly.

Table VII

Feed	Light Gasoline "B"	Light Gasoline "B"	Light Gasoline "B"
Run-Hours At Temperature	44-0	44-49	44-145
Temperature	800	800	850
WHSV	2.7	3.2	3.3
Pressure, psig	0.	0.	0.
Yields, wt. %			
Hydrogen	0.00	0.00	0.00
Methane	0.00	0.00	0.00
Ethylene	0.09	0.02	0.03
Ethane	0.00	0.00	0.00
Propylene	2.75	1.56	1.55
Propane	.02	0.00	0.00
i-Butane	0.15	0.15	0.12
n-Butane	0.51	0.44	0.41
1-Butene	0.85	0.67	0.76
iso Butene	2.49	1.48	1.58
t-2 Butene	1.42	1.35	1.23
c-2 Butene	1.10	0.97	0.95
Butadiene	0.00	0.00	0.00
Ratio Isopentenes/ Total Pentenes	0.71	0.69	0.68

Claims

1. A process for increasing iso-butylene yield and iso-pentene/total pentene ratio from naptha comprising contacting an olefinic naptha stream comprising C_5-C_9 olefins with a crystalline silicate catalyst at a pressure of less than 300 psig and a temperature of between about 500°F to about 900°F to produce a iso-butylene and iso-pentene rich product stream.

2. The process as recited in Claim 1 wherein the naptha is from an FCC.

3. The process as recited in Claim 1 wherein said product stream comprises iso-butylene, iso-pentene, saturated butanes and propylene.

4. The process as recited in Claim 3 wherein a stream comprising propylene is blended with said olefinic naptha stream.

5. The process as recited in Claim 3 wherein a stream comprising n-butylene is blended with said olefinic naptha stream prior to contacting said crystalline silicate catalyst.

6. The process as recited in Claim 3 further comprising separating the product stream into at least a propylene rich stream and a butylene rich stream comprising iso-butylene and n-butylene.

7. The process as recited in Claim 6 further comprising contacting said butylene rich stream with methanol in a MTBE unit to produce a MTBE product and a n-butylene rich stream.

8. The process as recited in Claim 3 further comprising separating the product stream into at least a propylene rich stream and a pentene rich stream comprising iso-pentene and n-pentene.

9. The process as recited in Claim 8 further comprising contacting said pentene rich stream with methanol in a TAME unit to produce TAME and a n-pentene rich stream.

10. The process as recited in Claim 7 or Claim 8 further comprising blending at least a portion of said propylene rich stream with said olefinic naptha stream at a point prior to contacting said olefinic naptha with said crystalline silicate catalyst.

11. The process as recited in Claim 7 further comprising recycling and blending at least a portion of said n-butylene rich stream with said olefinic naptha stream at a point prior to contacting said olefinic naptha with said crystalline silicate catalyst.

12. The process as recited in Claim 6 further comprising contacting a C_5-C_7 cracked FCC olefinic stream from the crystalline silicate reactor with at least a portion of said propylene rich stream in a disproportionation unit under disproportionation conditions to produce a iso-butylene rich stream and a gasoline stream.

13. The process as recited in Claim 6 further comprising contacting said butylene rich stream with water in a Tert-butyl alcohol unit to produce a TBA product and a n-butylene rich stream.

14. The process as recited in Claim 6 further comprising contacting said butylene rich stream with ethanol in a ETBE unit to produce a ETBE product and a n-butylene rich stream.

15. The process as recited in Claim 6 further comprising contacting said butylene rich stream within a dimerization unit to produce a polymerization gasoline and a n-butylene rich stream.

16. The process as recited in Claim 2 wherein the concentration of diolefins in said product stream is less than 0.05 wt%.

17. The process as recited in Claim 12 wherein said propylene rich stream is from a FCC unit.

18. The process as recited in Claim 1 wherein the catalyst is an intermediate pore zeolite of low acidity.

19. The process as recited in Claim 1 wherein the catalyst is silicalite with a silica to alumina ratio greater than 200:1.

20. The process as recited in Claim 17 wherein a portion of the propylene is substituted with FCC produced ethylene.

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 172 812 (EXXON) ---		C10G45/64 C10G51/02
A	WO-A-9 011 340 (MOBIL) ---		
A	US-A-4 865 718 (MOBIL) -----		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C10G
C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 JANUARY 1993	OSWALD DE HERDT